

Atomic Spectrometry for Elemental Analysis

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1. Introduction

Atomic spectrometry has been widely used for performing elemental analysis using absorption as well as emission phenomena. They are respectively referred to as atomic absorption spectrometry and atomic emission spectrometry. These are important instrumental techniques for both quantitative and qualitative analysis of metallic and nonmetallic elements in inorganic or organic materials. In this lecture we will discuss instrumentation of these techniques coupled with theoretical concepts underlying the phenomena to understand how these techniques work and we will take up a few applications using these techniques.

1.1 Atomic Absorption Spectrometry (AAS)

Wollaston in 1802 observed dark bands in the emission spectrum of the sun, which was marked with the beginning of the journey of atomic absorption spectroscopy. Kirchoff and Bunsen (1859) explained that the dark bands as observed by Wollaston were due to the absorption of emission radiation by ground-state gas-phase atoms in the sun. However, the absorption of radiation by atomic vapors was used as a quantitative analytical tool only in 1953 when Alan Walsh fabricated the first analytical atomic absorption spectrophotometer.

The technique of AAS consists of two steps: the conversion of an analyte molecule into its constituent gas-phase atoms (atomization), and the subsequent absorption of radiation by these free atoms. Essential components in AAS are schematically shown in Fig. 1.



Fig. 1. Essential components of AAS

1.1.1 Atomization

There are two methods for atomization process: (a) flame and (b) electrothermal method. Thermal energy is used for vaporizing the analyte material and for breaking the chemical bonds within the component molecules.

1.1.1A Flame Atomization

The processes that take place in flame atomization are given schematically in Fig. 2. Heating sample is most convenient for producing free atoms. In flame AAS, the sample meant for analysis is first dissolved in a suitable solvent. This solution containing the analyte of interest is first converted to an aerosol by spraying and then the aerosol is passed into the flame with a pneumatic nebulizer. Different types of pneumatic nebulizers and their function are shown in Fig. 3. Pneumatic nebulizers utilize the flame oxidant gas as a nebulization gas. The differential pressure of the oxidant gas, between the solution to be analyzed and the burner head, draws solution through a sample capillary into the oxidant gas stream as shown in Fig. 4.

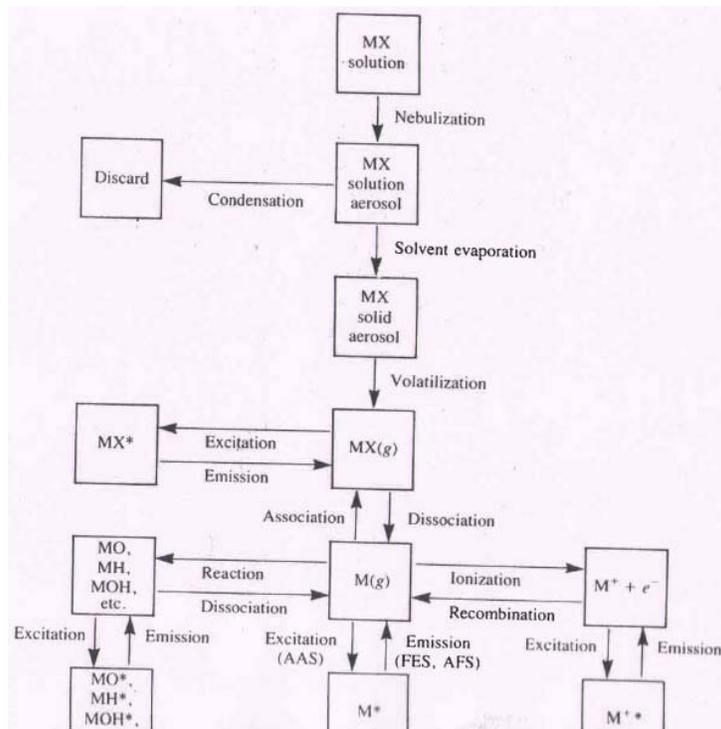


Fig. 2. Processes in flame atomization

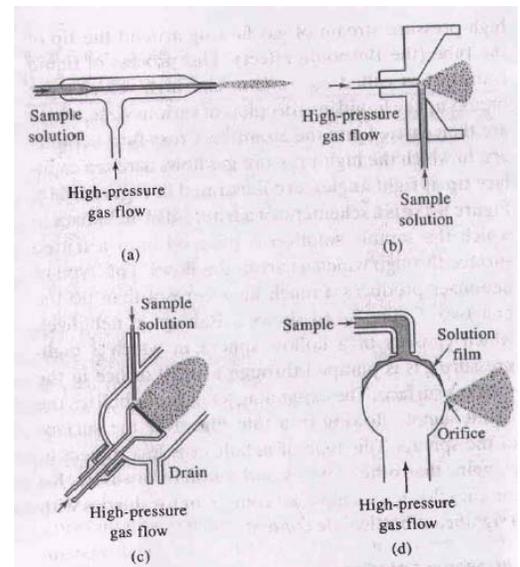


Fig. 3. Types of pneumatic nebulizers

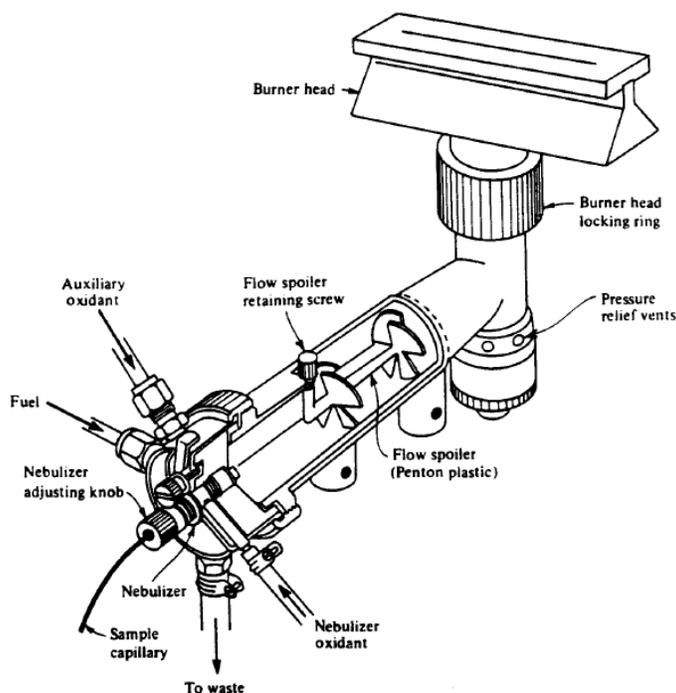


Fig. 4. Nebulizer and burner assembly as found in Perkin Elmer instruments

The stream passes through a small orifice to produce broad size distribution droplets. Larger sized droplets (more than 20 micron) are removed as they produce noise. Notably, only 10 % of the actual sample converted to aerosol could reach the burner and this is a limiting factor for analytical sensitivity of AAS. Further, flame gas expansion leads to dilution of aerosols and hence also limits the sensitivity of quantitation by AAS. Typical flame gases used in AAS are air-acetylene or nitrous oxide-acetylene and their maximum operating temperatures are respectively 2400°C and 2800°C. The burner path length for air-acetylene flame is typically 10 cm, whereas that for nitrous-oxide acetylene flame is only 5 cm. It is very important to take care to avoid any flashback to occur when using the nitrous oxide-acetylene flame. The flame temperature is very important to dictate the number of atoms in the excited state, which depends on the Maxwell-Boltzmann distribution. Note, the number of atoms in the excited state is far less than the atoms in the ground state. But we have to remember that the AAS signal is not due to the thermal excitation but it is due to excitation of atoms from ground state to the excited state due to absorption of radiation. Therefore thermal means for excitation contribute to interferences in the analysis. We have to also realize that the atomization by thermal method, does not lead to homogeneous distribution of atoms in the flame, rather the distribution of atoms would depend on the gradient in the flame temperature. To achieve maximum analytical sensitivity, the radiation from the line source should pass through the area of the flame that contains the greatest number of free atoms. This condition is met by optimizing the height and alignment of the burner head relative to the radiation beam as it passes through the flame parallel to the major axis of the burner.

1.1.1B Electrothermal Atomization

The electrothermal atomization was developed to overcome the sensitivity problems associated with flame AAS. The nebulizer and burner assembly of a flame AAS instrument is replaced with an electrothermal atomizer. An electrothermal atomizer comprises a graphite furnace (Fig. 5), carbon rod, and tungsten ribbon atomizers. In these atomizers, a 5 to 50 mL aliquot of the sample is placed in the resistively heated element and then heated stepwise to the temperatures conducive to gaseous atom formation. A typical heating program involves a solvent evaporation step (110°C), an ashing step for the removal of any volatile organic materials (450–900°C) and a 5 to 10 second atomization step (2000–3000°C). The entire heating cycle can be accomplished in less than one minute.

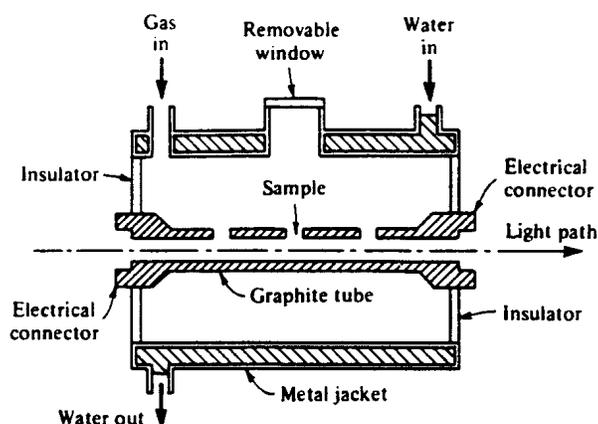


Fig.5. A graphite furnace electrothermal atomizer

The electrothermal atomizer increases analytical sensitivity of a few orders of magnitude over flame AAS. Typically, analytes present in picogram quantities can be determined by electrothermal AAS. The reasons for improved sensitivity are: (a) samples are not diluted by flame gases; (b) it does not depend on nebulization efficiencies. More interestingly, solid samples can be directly measured by electrothermal atomizer.

On the other hand, electrothermal atomizer suffers from various limitation, and the major limitation is the reduced precision of the analytical results obtained, compared to flame AAS. This is due to short lifetime of the free atoms (0.01 seconds) in the optical path for electrothermal analyzer, whereas the flame atomization continuously nebulizes free atoms to the flame for analysis and the signal can be averaged over a long period of time.

1.1.2 Excitation Source

The full width at half-height of the absorption line produced by either flame or electrothermal atomization as measured by emission spectroscopy is approximately 0.002 nm. The line broadening could take place by either of the following processes or by the combination of them, e.g., natural line broadening, pressure, resonance, and Doppler

broadening. It is very important that the line sources used for excitation must be stable and narrower than the full width at half-height of the absorption of the analyte to obtain both sensitivity and selectivity.

Line sources typically used include the hollow cathode lamp and the electrodeless discharge lamp. With proper instrumental design, even continuum sources can be used. We will discuss here only the hollow cathode lamp.

1.1.2A Hollow Cathode Lamp

Schematic diagram of a typical hollow cathode lamp (HCL) is given in Fig. 6. A potential of 350V to 500V (producing a current of 1 to 50 mA) is placed across the cathode and anode terminals. The element selectivity of the HCL is achieved by fabricating the cathode from, or coating the interior of the cathode with, the element of interest.

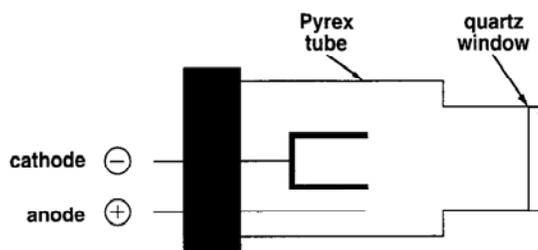


Fig. 6. Schematic diagram of a hollow cathode lamp

The interior of the tube is evacuated and filled with an inert gas, such as neon. Under the applied potential, the neon atoms ionize at the anode and are accelerated toward the cathode. The kinetic energy of the accelerated neon ions fall on cathode and upon impact, it causes sputtering of metal atoms from the cathode surface into the gas phase, collides with neon gas and ionizes the gas. The sputtered metal atoms undergo collisions with other neon ions, and produces excited state metal atoms. These metal atoms emit radiation at their characteristic wavelengths during their relaxation process to ground state. The full width at half-height of the atomic line produced is approximately 0.0002 nm, and therefore all of the radiation produced is available for absorption by the atomized sample.

The intensity of the atomic line radiation produced depends on the number of sputtered metal atoms, which depends on the kinetic energy of the neon ions, which, is corresponds to the lamp current. Consequently, a higher lamp current produces greater spectral line intensity from the source, and provides a greater analytical sensitivity. However, at high lamp currents, an excess of metal atoms is sputtered from the cathode surface resulting into a dense cloud of metal atoms which can absorbs radiation emitted from nearby excited-state metal atoms. This process is called Self-absorption and is a parameter for reduced sensitivity.

1.1.3 Background Correction

There are three primary methods for background correction are (1) the addition of a broadband or continuum source, (2) pulsing the HCL source, and (3) application of the Zeeman effect to the source or sample.

As the free atoms are kept at a high flame temperature, these atoms would tend to radiate, which is similar to continuum radiation. In order to take into account of the background contribution due to continuum radiation, a continuum source (hydrogen or deuterium lamp) is incorporated along with hollow cathode lamp. At the wavelength produced by the HCL, the absorption is due to both atomic and non-atomic species distributed in the flame. Over the bandpass of the monochromator, the absorption of the continuum source radiation is attributable to primarily non-atomic species. The difference between the absorption due to the hollow cathode lamp and the absorption due to the continuum source represents the absorption due to atomic species in the flame. The background can be estimated by using source modulation technique.

1.1.4 Interferences

There are four types of interferences, e.g., chemical, ionization, matrix and spectral interferences. These interferences will be discussed in the lecture.

In addition, it is important to mention that arsenic determination by conventional AAS is a challenge as it suffers from poor sensitivity. In this regard, hydride generation technique can be used for achieving several folds better sensitivity. A schematic diagram is given as Fig. 7 to demonstrate the instrumentation needed for hydride generation.

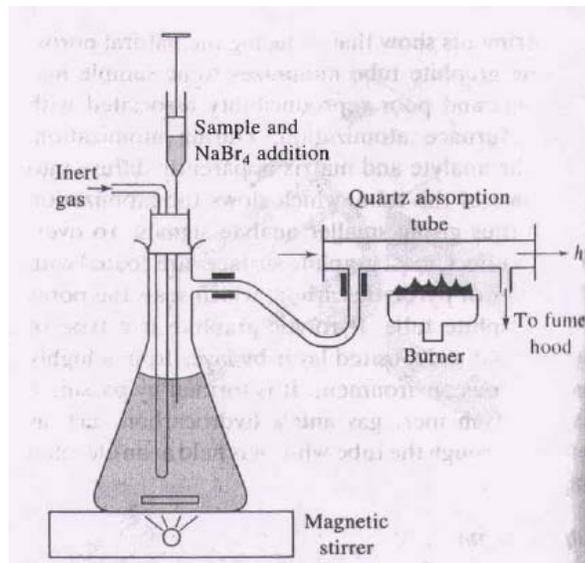


Fig. 7. Hydride generation and atomization in AAS

1.1.5 Quantitation

The quantitation by AAS is based on Beer- Lambert principle, i.e., Absorption is proportional to the concentration of the analyte. However, sample preparation plays a significant role for achieving better results using AAS.

1.2 Inductively Coupled Plasma (ICP)

This is a part of atomic emission phenomenon. The demand here is to populate the excited state from where the atoms de-excite and the corresponding emission radiation is measured to quantify the elemental concentration. As we have discussed in previous section, that the flame temperatures used in AAS are not suitable for exciting the atoms in sufficient numbers to achieve any analytical sensitivity, it indicates that much higher temperature would be required for studying emission process. Among various methods, the inductively coupled plasma source is an exciting one. The inductively coupled argon plasma torch (as shown in Fig. 8) is a special type of plasma that derives its sustaining power by induction from high frequency magnetic field. Initially argon gas passes through a 25 mm quartz tube, upon emerging at the tip, it is surrounded by an induction coil. An ac current flows through the coil at a frequency of about 30 MHz which gives a power of 2 kW.

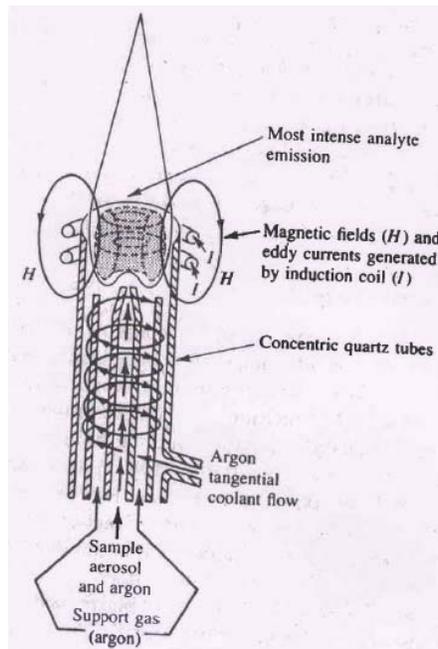


Fig. 8. Schematic configuration of ICP

The argon gas stream (support gas) that enters the coil is initially seeded with free electrons from Tesla discharge coil. These see electrons quickly interact with magnetic field of the coil and gain sufficient energy to ionize argon atoms, by collisional excitation. Cations and electrons generated by the initial Tesla Spark are accelerated by the magnetic field in a circular flow perpendicular to the stream that emerges from the tip of the torch. Reversal of the direction of the current in the induction coil reverses the

direction of the magnetic field applied to the mixture of atoms, ions and electrons. The fast-moving cations and electrons, known as eddy current, collide with more argon atoms to produce further ionization and intense thermal energy. A flame shaped plasma forms near the top to the torch and the temperature in the plasma ranges between 6000 and 10000 K.

The emission spectrum of respective elements can be then detected using an optical measurement system like photomultiplier tube or photodiode, or by attaching a mass spectroscopy system to the ICP.

1.3 Conclusion

The principles of atomic spectroscopy coupled with instrumentation protocols have been useful to measure concentration of elements present in samples at trace to ultra trace levels.

1.4 References

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